

## **SMART COATING FOR CORROSION INDICATION AND PREVENTION: RECENT PROGRESS**

Wenyan Li, Paul Hintze, Luz M. Calle, Jerry Buhrow and Jerry Curran  
Corrosion Technology Laboratory  
Kennedy Space Center, FL 32899  
[Wenyan.Li-1@nasa.gov](mailto:Wenyan.Li-1@nasa.gov)  
[Luz.M.Calle@nasa.gov](mailto:Luz.M.Calle@nasa.gov)

A. J. Muehlberg, V. J. Gelling, D. C. Webster, and S. G. Croll  
Coatings and Polymeric Materials  
North Dakota State University  
1735 Research Park Drive, Fargo, North Dakota 58105

F. Contu and S. R. Taylor  
University of Texas Health Science Center  
6516 MD Anderson Blvd, Houston, TX 77030

### **ABSTRACT**

The authors are developing a smart coating system based on pH-triggered release microcapsules. These microcapsules can be incorporated into various coating systems for corrosion detection, protection and self-repair of mechanical coating damage. This paper will present the results from progress made to date in the controlled release properties of these microcapsules as well as in their corrosion indication and corrosion inhibition function.

**Keywords:** smart coating, corrosion detection, corrosion prevention, controlled release

## INTRODUCTION

Corrosion is a costly problem for military operations and civil industries. Localized corrosion can cause catastrophic failures in pipes and tubing. One way of preventing these failures is with a coating that can detect and heal localized corrosion.

pH and other electrochemical changes are often associated with localized corrosion, so it is expected that materials that are pH or otherwise electrochemically responsive can be used to detect and control corrosion. Various pH and electrochemically responsive materials and their potential applications in corrosion control coatings can be found in our previous review.<sup>1</sup> Both color and fluorescent pH indicators have been incorporated into coating systems for corrosion sensing applications. Although there are still technical challenges associated with corrosion indicating coatings, they are showing great promise for industrial applications.<sup>2-18</sup> Conductive polymers and surface modified nanoparticles have been studied as potential materials for inhibitor controlled-release applications.<sup>19-24</sup>

Self healing coatings are another new development in material design that is important to corrosion control.<sup>25</sup> Among the chemistries that have been proposed, a few involving using mechanically breakable microcapsules.<sup>26-28</sup>

The authors at NASA Kennedy Space Center have developed a controlled-release system that combines the advantages of corrosion sensing and corrosion protection functions using pH-triggered release microcapsules.<sup>1,29,30</sup> The core component of this technology is a pH sensitive microcapsule. The microcapsule wall will break down and release its contents under basic conditions, which correspond to the pH conditions at the cathodic site of corrosion (as shown the figure below).

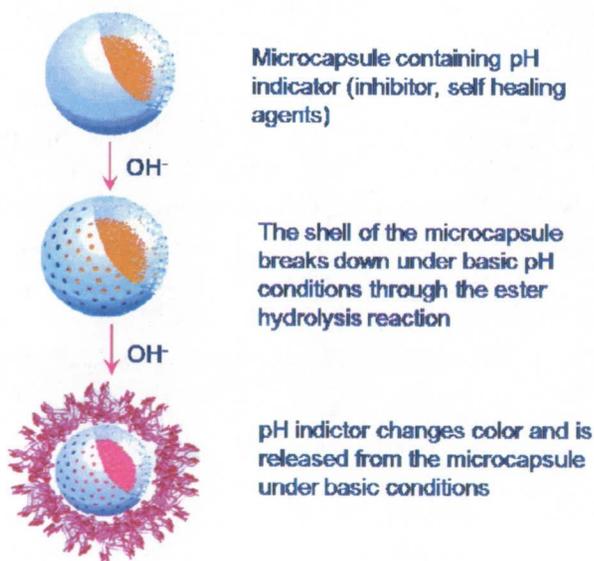


Figure 1. The central component of the smart coating system: pH sensitive microcapsules which break down under basic pH conditions.

This microcapsule approach has many advantages. It is very versatile, can be used to encapsulate an unlimited number of materials, in both solid and liquid phase. For corrosion applications, various compounds, such as corrosion indicators, inhibitors, self-healing agents, and dyes can be encapsulated. These microcapsules can be incorporated into various coating systems for corrosion detection, protection and self-repair of mechanical coating damage (Figure 2). The versatility of the design is of special interest in corrosion inhibition applications. Almost all corrosion inhibitors are chemically active reagents. Very often, the reactivity that makes them effective corrosion inhibitors also causes them to be environmentally unfriendly, such as in the case of hexavalent chromates. Because of this, research for new and environmentally friendly corrosion inhibitors is an on-going effort in the corrosion protection industry. After a new inhibitor is developed, it can take a long time to incorporate it into a paint formulation. A smart coating that includes encapsulated inhibitors, can shorten this long reformulation process for new inhibitors by simply changing the core content of the microcapsules.

The pH-controlled release microcapsule design has an advantage over chemically inert microcapsules in that it has a true controlled-release function for corrosion application. Regular microcapsules release their contents when they are mechanically broken. pH sensitive microcapsules release their contents when corrosion occurs. Mechanical damage in a coating is one of the important causes for corrosion of base metals; however, it is not the only one. Many forms of defects in coatings, such as air bubbles, uneven thickness, permeation, delamination, porosity or edge effects, will result in poor corrosion protection. pH-sensitive microcapsules will release their content when corrosion occurs, even in areas where there has not been any mechanical damage.

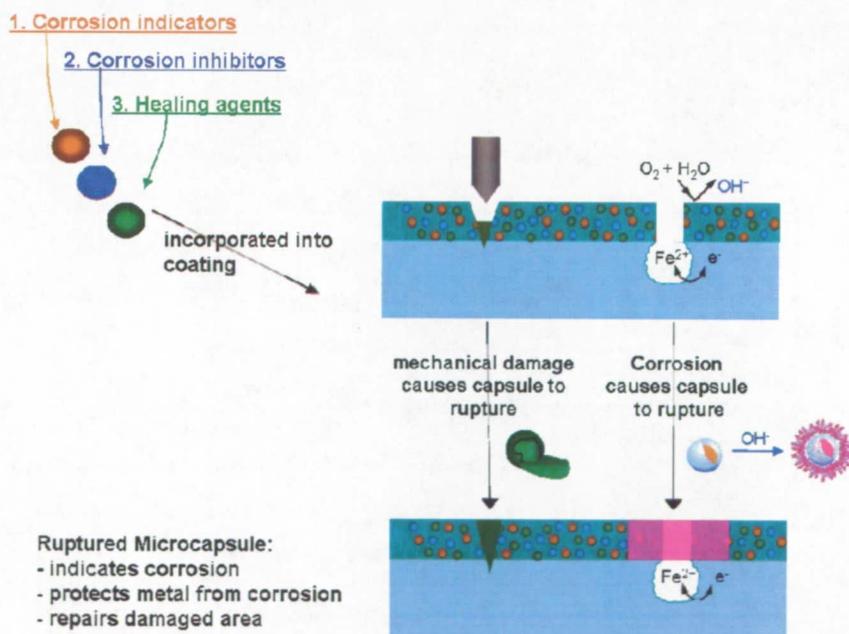


Figure 2. Smart coating with pH sensitive microcapsules for corrosion detection and protection applications.

This paper will report the recent progress made in the encapsulation process, the characterization of these microcapsules, such as their mechanical and thermal properties, as well as results showing the controlled release function. Microcapsules were incorporated into paint formulations, and the corrosion protection of these paints were tested using electrochemical methods.

### MICROENCAPSULATION PROCESS

The development of encapsulation techniques is of critical importance because the pH sensitive microcapsule is the key component of the smart coating design. There are several methods available to make microcapsules such as spray drying, emulsion polymerization, and interfacial polymerization. We have been successful in using interfacial polymerization to encapsulate various compounds of interest to this project. There are two main steps in the process we have chosen: microemulsion formation and microcapsule wall formation through interfacial polymerization. This technique can be used to form both oil core and water core microcapsules. Figure 3 shows a schematic representation of the steps involved in forming oil core microcapsules: the microemulsion is formed by adding the oil phase (with prepolymer, shown in yellow) to the water phase (with surfactant, shown in blue) and mixing; the last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization. Figure 4 shows a schematic representation of the steps involved in forming water core microcapsules: in this case, the microemulsion is formed by adding water (shown in blue) to the oil (with prepolymer and the surfactant, shown in yellow) followed by mixing; the last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization.

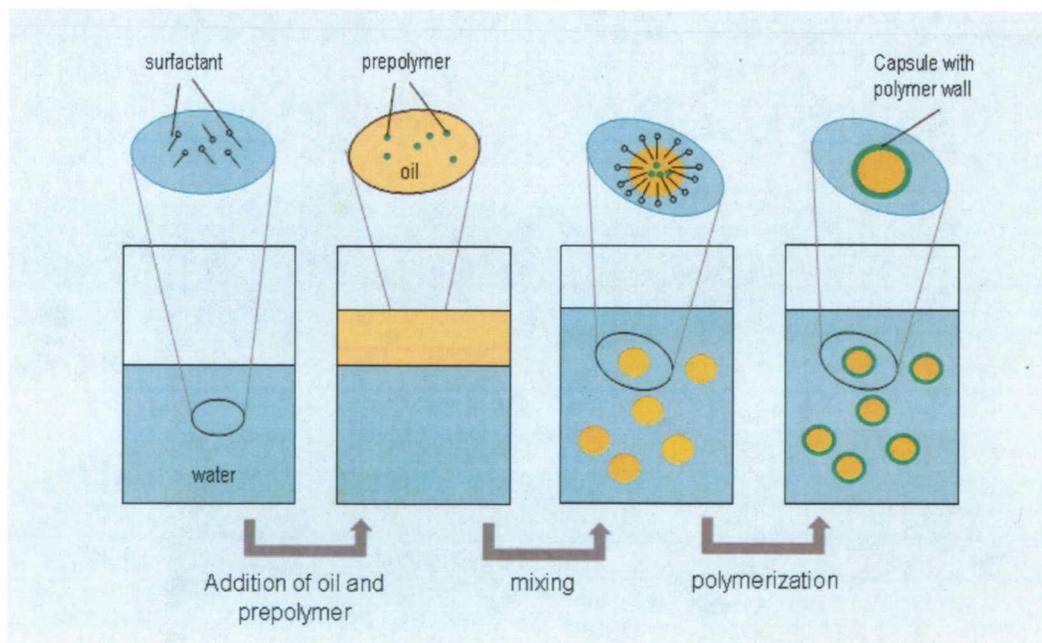
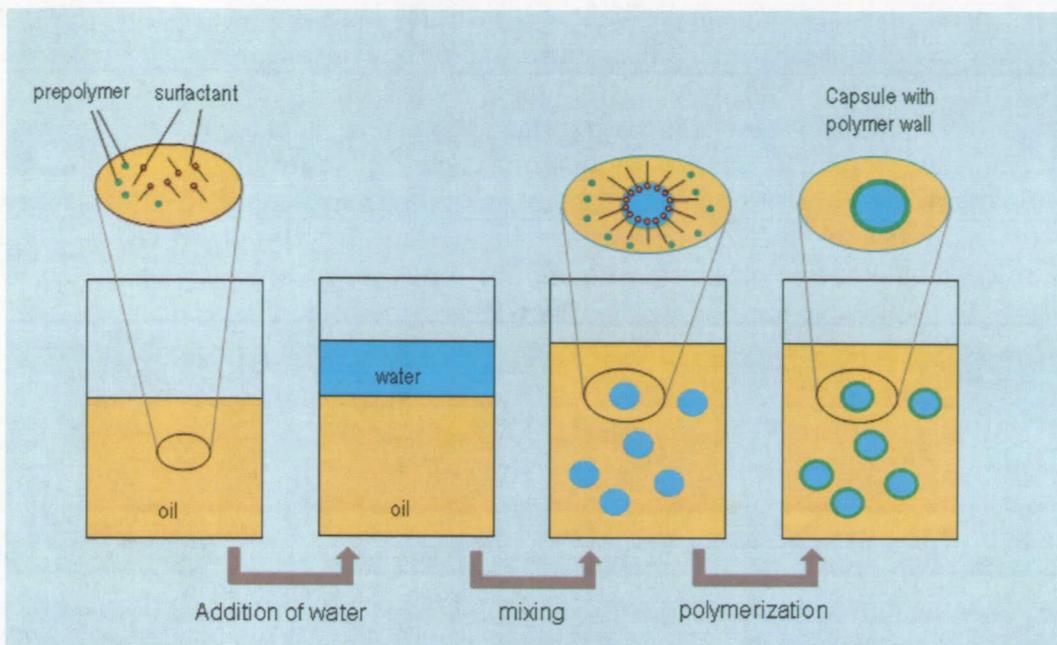


Figure 3. Schematic of the steps involved in the interfacial polymerization of oil-in-water microemulsion process for making oil core microcapsules. Oil is shown in yellow and water in blue.



**Figure 4. Schematic of the steps involved in the interfacial polymerization of water-in-oil microemulsion process for water core microcapsules. Oil is shown in yellow and water in blue.**

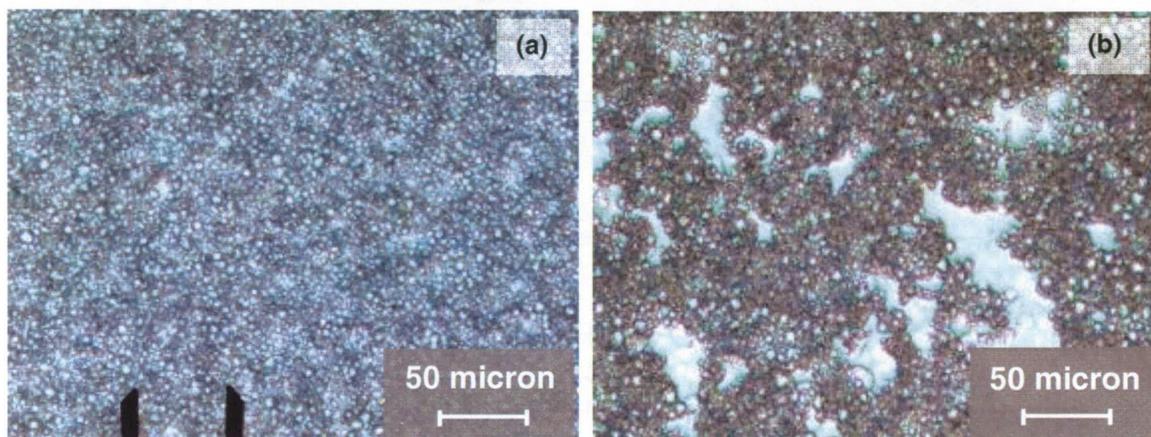
Methods have been developed for the encapsulation of water soluble and insoluble compounds. To tailor these processes for encapsulating corrosion inhibitors and indicators, various indicators and inhibitors were selected and tested for their indicating and inhibiting functions respectively. The solubility of indicators and inhibitors have been surveyed or tested, to find a suitable method to determine their encapsulation. Water-soluble compounds will be encapsulated into water core microcapsules and the water insoluble compounds will be encapsulated into oil core microcapsules. When a compound does not have sufficient solubility in either the water core or the oil core microcapsules, a cosolvent is chosen to improve the solubility and facilitate the encapsulation process.

These methods have also been optimized in order to get desired capsule size, size distribution, wall thickness, pH sensitivity. Further optimization was carried out to form free-flow powders for powder coating applications.

### **Optimization of encapsulation techniques for water core microcapsules**

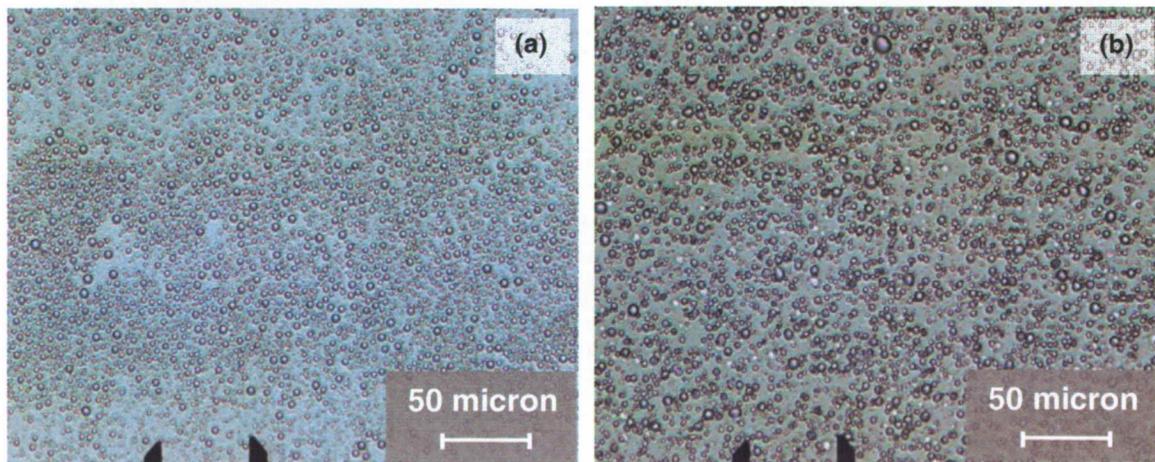
In order to encapsulate water soluble as well as water insoluble compounds, it is important to have a working formula for water core and oil core microcapsules. Water core microcapsule synthesis was found to be considerably more challenging than that of oil core. It is comparatively easier to make monodispersed oil core microcapsules of desired size than to make water core microcapsules due to their tendency to form clusters (Figure 5). This problem was observed during the initial attempts at their synthesis and had to be solved before the microcapsules are to be incorporated into paint formulations.

In general, it is easier to make stable oil-in-water microemulsions (Figure 5a) because there are more options of surfactants to stabilize the oil-in-water emulsions. This is due to the type of intermolecular interactions such as columbic interactions (in the case of ionic surfactants) or dipole-dipole interactions (for non-ionic surfactants). These interactions are strong and keep the microemulsion droplets from coalescing. In the case of water-in-oil emulsions, the major sources of interactions are through London dispersions or simple steric effects between the surfactant tails. These interactions are weak and are not as effective at keeping the microemulsion droplets from clustering (Figure 5b). However, it is possible to obtain water-in-oil emulsions that are stable long enough for the wall polymerization to occur.



**Figure 5. (a) Oil-in-water microemulsion showing a homogenous size distribution and a good dispersion (b) An early water-in-oil microemulsion formula showing some clustering.**

In order to solve the clustering problem, a matrix study was carried out to find an optimized water/oil/surfactant combination for water-in-oil microemulsion formation. This effort was successful in identifying a new water-in-oil emulsion formula, which forms a stable emulsion with monodispersed size distribution and dispersed size of 1 to 5 micron. This new emulsion formula was applied to resolve the clustering (or dispersion) problem of the water core microcapsules, and these efforts were successful. Various water-soluble corrosion inhibitors were encapsulated using this approach, such as  $\text{Ce}(\text{NO}_3)_3$  and  $\text{NaMoO}_4$ , as shown in Figure 6.



**Figure 6. The watercore microcapsules made from water-in-oil emulsion showing good dispersion: (a)  $\text{Ce}(\text{NO}_3)_3$  containing microcapsules and (b)  $\text{NaMoO}_4$  containing microcapsules.**

## Optimization of encapsulation techniques for oil core microcapsules

In general, it is relatively simple to form a stable oil-in-water microemulsion, so the early optimization of oil core microcapsules has concentrated on controlling capsule size and improving the size distribution, **Error! Bookmark not defined.** as shown in Figure 7.

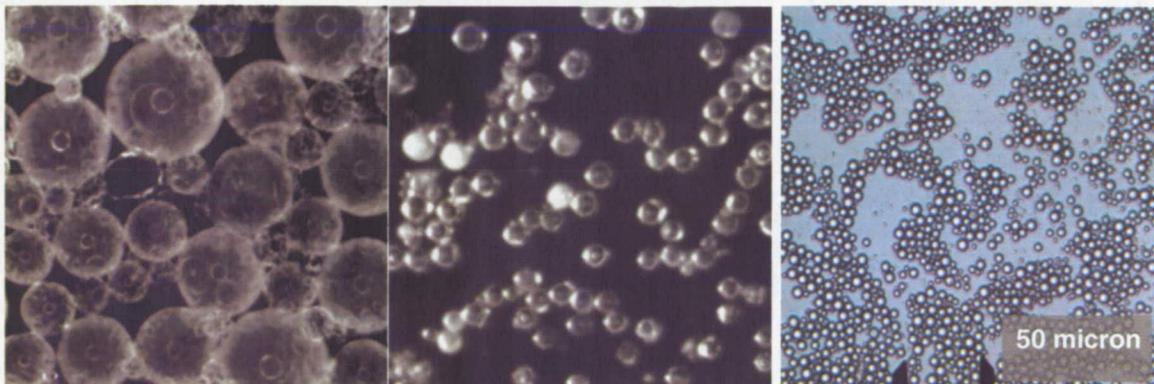


Figure 7. Oil Core Microcapsules of Different Sizes.

Early optimization of oil core microcapsules also included adjusting the pH sensitivity of the wall material, which involved the adjustment of wall thickness as well as the chemistry of the polymerization reaction. [reference] Recently a new oil-in-water emulsion formula was adopted to synthesize oil core microcapsules that could be easily processed to form a free flowing powder. The older formula formed an extremely stable emulsion. It was very difficult to remove the microcapsules from the emulsion, posing great difficulty in the washing and drying process. Microcapsules made in this fashion were typically added to a paint as an emulsion, without much drying. The new emulsion formula provides the optimized stability for polymerization, as it produces homogenous microcapsule size (from 2 to 5 micron). The capsules can be easily washed and dried into free flowing powder, as shown in the figure below. Various corrosion indicators and dyes were encapsulated into oil core microcapsules, and then were separated from the dispersing medium (water and surfactants, etc.) through centrifuging. These microcapsules were washed thoroughly with water till they are clean. Then the microcapsules were left to dry at room temperature. The free flowing powder was obtained after minimal grinding and sifting.



Figure 8. Oil Core Microcapsules in free flow powder forms. The core contents of these microcapsules are Rhodamine B (on the left), Phenolphthalein (in the middle), and a universal pH indicator (on the right).

## CONTROLLED RELEASE OF THE MICROCAPSULES

As indicated earlier, the pH sensitivity of the microcapsule is the core feature of these smart coatings. The asensitivity of the microcapsule wall material to basic pH conditions and the ability of the microcapsule to release its contents when needed has been evaluated through different test methods.

### pH Controlled Release Properties of the Microcapsules

To observe how these microcapsules react under basic conditions, some microcapsules containing phenolphthalein were observed with an optical microscope while a sodium hydroxide (NaOH) solution was added to adjust the pH to about 12. Figure 9 shows time lapse images of a single capsule reacting to the basic pH conditions. Soon after the NaOH solution was added, it started to penetrate the microcapsule wall, indicated by the color change inside the microcapsules (Frames b-d). In frame 9e, the microcapsules begins to slowly release its contents. The contents continue to be released until frame 9i, when they dissipate into the solution. The microcapsule wall eventually collapses as shown in frames 9i thru 9n.

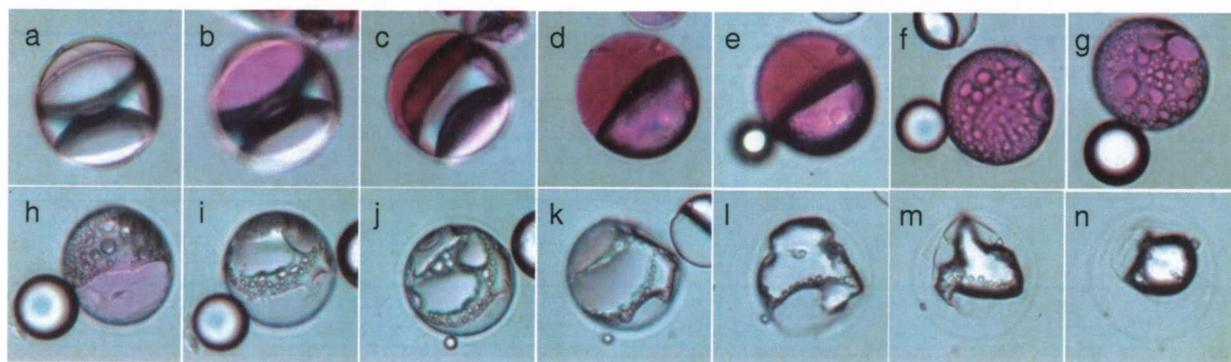


Figure 9. Time lapse pictures of a microcapsule breaking down under basic pH conditions.

In order to further verify and qualify the controlled release property of these microcapsules, water-core microcapsules containing cerium nitrate were exposed to alkaline solutions and the release of cerium was monitored over time. In these experiments, 0.2 g of microcapsules was placed in solutions with a pH of either 7 or 14. The concentration of cerium was measured just after mixing, and after one and two hours of exposure. The cerium was sampled by filtering the mixture through a 0.45  $\mu\text{m}$  filter. The filtrate was acidified and the concentration of cerium was measured with an inductively couple plasma (ICP) instrument. The results are shown in Table 1. The very low amount of cerium detected in the pH 7 controls shows that most of the cerium is inside the capsule and that it does not leach from the capsule over this time frame. The cerium concentration increases very quickly in the pH 14 solutions and show that the capsules have released their contents within 2 hours. Measurements at longer exposure times were unsuccessful because the polymer degraded and formed a film that prevented accurate sampling.

Elapsed Time (hours)	Concentration of Cerium	
	pH 7 solution	pH 14 solution
0	0.15	2.07
1	0.18	6.7
2	0.23	6.9

**Table 1: Concentration of Cerium released from microcapsules in pH 7 and 14 solutions over time**

### **Controlled Release of Microcapsule Content at the Onset of Corrosion**

It was clear from the above experimental results that these pH sensitive microcapsules will break down under basic condition and release its content at various basic conditions, but would they deliver their content “on demand” when localized corrosion occurs? Although this is a logical conclusion based on the well known fact that local pH changes are normally associated with corrosion (the oxygen reduction reaction result in basic pH at cathodic site), the direct evidence is still the most convincing. In order to provide this direct evidence, a galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was set up and immersed in gel with microcapsules containing phenolphthalein, as corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and progress of corrosion (as shown in the figure below).



**Figure 10. A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was set up and immersed in gel with microcapsules containing a corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and progress of corrosion.**

This test provided the direct evidence that these microcapsules can release their content “on demand” at the onset of corrosion. It also shows that encapsulated pH indicators can serve as a sensitive corrosion indicator. The color change, indicating cathodic activity, can be observed as early as 0.5 hour after exposure began. Rust was not visually observed until after 4 hours of exposure.

## PAINT FORMULATION WITH MICROCAPSULES

The microcapsules have been incorporated into some initial paint formulations. While we are still in the early phase of the development stage, there are many encouraging results. As mentioned earlier, one of the advantages of this smart coating system is its versatility. The microcapsules can be incorporated into many types of coatings, such as epoxies, acrylics, urethanes, powder coatings, or used simply as additives for both liquid and powder coating applications. Thus, it is of critical importance to investigate the compatibility between the paint components and the microcapsules.

We performed tests to look at the compatibility between the microcapsule and some widely used paint solvents and some existing paints. Initial experiments to determine the compatibility of the microcapsules with paint application processes were also performed. Results from these tests are presented here and can provide useful information for future paint formulation development.

### Compatibility Study between the Microcapsules and Paint Formulation

There are three main components in a paint system:<sup>31</sup> pigment, binder, and solvent. There are two main factors to be considered for compatibility between the microcapsules and the paint components. The first is solvent compatibility. This refers to whether or not the paint solvents will destroy (dissolve) or damage (degrade) the microcapsule wall. The second is binder compatibility, or determining if the binder reacts with the microcapsule. Binder compatibility issues should only arise in the case of convertible coatings, which undergo a chemical reaction when curing. The binders in non-convertible coatings are not reactive, and should therefore be compatible with the microcapsules. Normally, pigments are generally designed to be inert to other coating formulation components and should have no effect on the microcapsule wall integrity.

#### *Solvents Compatibility Test*

The solvent compatibility test consisted of placing some of the microcapsule wall material into a paint solvent, and observing if the wall materials was degraded or dissolved. Several paint solvents were selected to represent the most often used solvent families: toluene, ethanol, methyl ethyl ketone (MEK), 2-butoxy ethanol, n-butyl acetate, and water. The microcapsule wall material was synthesized and ground into fine powder before placing in the solvent. The solubility of the wall material in selected solvents was tested at room temperature and at a slightly elevated temperature, 50°C (based on the possible temperature range of paint application). There was no indication of dissolution of the wall material in any of the solvents in an hour. The mixtures were left at room temperature for a week, and no change was found when they were observed again. The solubility testing results showed that the microcapsule wall material is not soluble in any of the selected solvents.

### Formulation Stability Test

There are several concerns regarding the incorporation of microcapsules into a paint. One concern is that they could affect the (suspension) stability of existing paint systems. If the microcapsules were incompatible with the paint system, the paint system might undergo phase separation (binder, solvent, pigment) before application of the paint could be completed. This study was performed to determine the general compatibility of the microcapsules with typical resins. Three water-based resins (alkyd, acrylic, and polyester) and two solvent-based resin (acrylic and polyester) were selected for this test.

Empty oil core microcapsules, oil core microcapsules with corrosion indicators, and water core microcapsules with corrosion inhibitor were used in this study. For each compatibility test, the resin was brought to a casting viscosity of around 300-400 centipoises. This was done with the manufacturer suggested compatible solvent. After the ideal viscosity was obtained, a suspension of microcapsules in water was mixed into the resin formulation at 15 wt% solids and poured into glass vials. Images of the vials were captured immediately after pouring and after 3 and 24 hours. The mixtures were observed to see if phase separation would occur. If the mixture showed no sign of phase separation, for a sufficient period of time suitable for paint application (2 to 4 hours), this indicated that there is good compatibility between the microcapsule and the resin formulation.

The results of the compatibility study from are summarized in Table 2. They showed that oil core microcapsules are compatible with water based paints while water core microcapsules are compatible with solvent based paints. These results were expected by considering the fact that the oil core microcapsules are made from oil-in-water microemulsion and thus are expected to be compatible with another suspension system with water as the continuous phase (water based paint). Similarly, water core microcapsules are compatible with solvent based paints and oil core microcapsules are incompatible with solvent based paints.

**Table 2. Compatibility of microcapsules with commercial resin formulations.**

Oil/Water Base	Resin Type	Microcapsule Tested	
		Oil core	Water Core
Water Based	Alkyd Resin	Compatible	
	Acrylic Resin	Compatible	
	Polyester Resin	Compatible	
Solvent Based	Acrylic Resin	Incompatible	Compatible
	Polyester Resin		Compatible

For film formation, the microcapsule formulations only need to stay compatible for several hours before application, although better stability is desirable. The study showed that each system tested with the correct microcapsule system would most likely stay suspended in solution well beyond 24 hours after stirring, thus suggesting that it is likely that there will be no problems in the future formulating with similar resins.

### Microcapsule Effect on Coating Adhesion

The adhesion of paint containing microcapsules was measured to determine if the microcapsules would negatively affect this physical property. Sandblasted carbon steel test panels (6×4 inch<sup>2</sup>) were coated using four representative paint systems: Acrylic, Epoxy, Polyurethane, and Siloxane. These panels were tested for adhesion with a PATTI (Pneumatic Adhesion Tensile Testing Instrument) tester according to ASTM standard D4541-85(89). These results are shown in Figure 11. The results showed that incorporation of microcapsules into the representative paint systems has less than a 15% effect on the paint adhesion properties. No attempt to optimize the microcapsule loading was made in these tests.

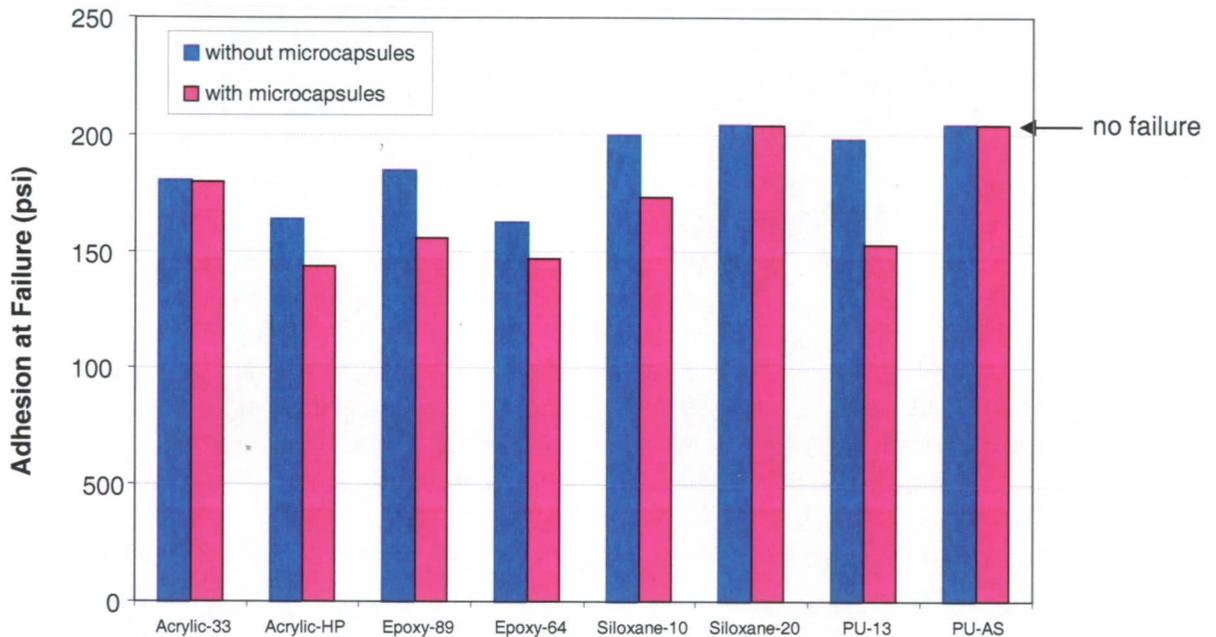


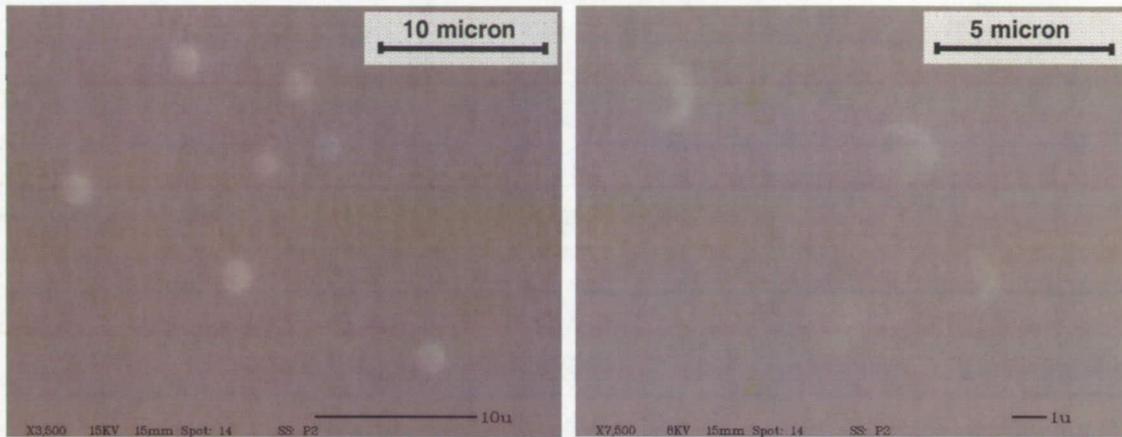
Figure 11. PATTI adhesion test results of various commercial paint systems.

### Paint Formula and Coating Process Effect on Microcapsules

The microcapsules must be compatible with the coating process. For example, it is desirable to know if the microcapsules will survive the high shear mixing and coating application processes such as spraying. It is possible that they will get broken in the process, or that they might clog the spray gun and not be sprayed properly. If the microcapsules survive the chemical environment of paint formulations and mechanical impact during paint application, they still might not keep the same functionality in dried paint that they exhibited in the colloid system or dried powder form. These concerns are related to the size and mechanical strength of the microcapsules as well as to the chemical stability of their structure. To address these concerns, oil core microcapsules were incorporated into selected existing paint systems that were applied to different metal substrates by brush painting and spray coating processes. Initial testing shows

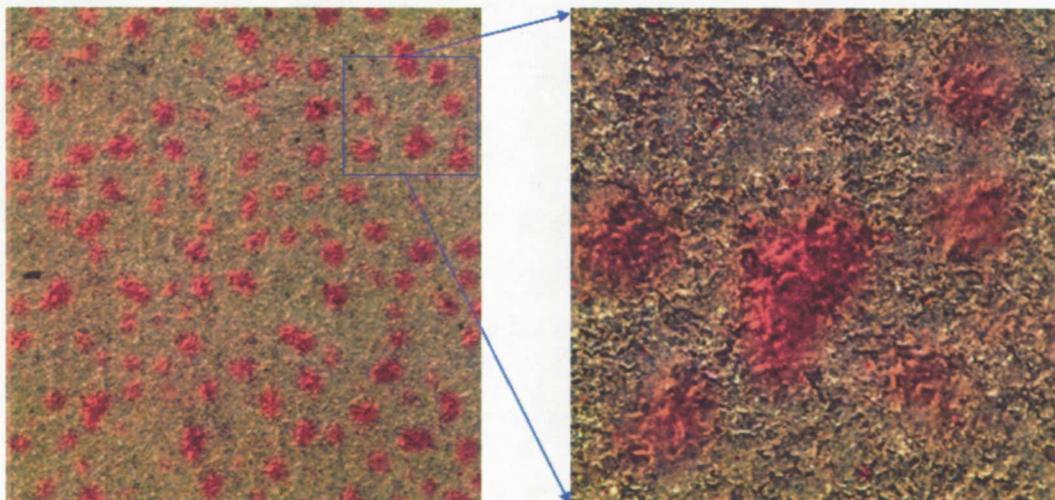
that the microcapsules can survive in some paint formulations and regular coating application process without losing the functionality for which they were designed.

The SEM images in Figure 12 show that microcapsules remain intact when they are incorporated into an Epoxy coating. The microcapsules were dispersed in a solvent mixture and then the epoxy, Epon 828, was added into the dispersion. Lastly, the amine curing agent, bis(p-aminocyclohexylmethane (PACM), was added. The epoxy was applied by brushing onto the AA2024-T3 panels, which were sandblasted and degreased before coating application. The coatings were allowed to cure under ambient conditions for 48 hours before any testing.



**Figure 12. Microcapsules appear dispersed and stable inside the epoxy amine coating.**

Another test showed that microcapsules with an average size of 20 microns or smaller can withstand conventional high shear stirring often used in paint mixing. The mixed formulation was applied to carbon steel panels by spraying using a commercially available high volume, low pressure (HVL) spray gun. The pH sensitivity of the microcapsules in dry paint was also tested. Figure 13 shows the vivid color changes observed when the microcapsules in the dry paint were exposed to basic pH conditions.



**Figure 13. Color change observed when microcapsules in dry paint were exposed to basic pH conditions.**

## Electrochemical and Salt Spray Testing

Electrochemical impedance spectroscopy (EIS) and salt spray testing (ASTM B117) were used to evaluate the corrosion resistance of paints with incorporated microcapsules. Microcapsules containing  $\text{Ce}(\text{NO}_3)_3$  or  $\text{NaMoO}_4$  were incorporated into an epoxy and coated on AA2024 for testing. Coated panels with microcapsules containing an inhibitor were compared with coatings containing empty microcapsules and coatings containing no microcapsules.

The low frequency impedance, which has an inverse relationship to the barrier protection provided by a coating, was determined by EIS for all samples and is summarized in Figure 14. From Figure 14, one can see that there are consistent differences between the samples when comparing the low frequency impedance. The samples containing the water-core microcapsules with  $\text{Ce}(\text{NO}_3)_3$  were able to maintain a relatively high value of low-frequency impedance throughout the immersion time. In comparison, the control coating which contained 40% of the blank oil-core microcapsules displayed a decrease in impedance with respect to immersion time. This is to be expected, as blank oil-core sample contains no corrosion inhibitor and the empty capsules would likely increase coating porosity. Such a result is often observed for a barrier-type coating placed under immersion when no corrosion inhibitors are present.

Interestingly, coating samples with water-core microcapsules containing  $\text{Na}_2\text{MoO}_4$  displayed relatively low initial low-frequency impedance when compared to the blank oil-core and  $\text{Ce}(\text{NO}_3)_3$  enclosed water-core microcapsules. Such a result is often observed when examining uncoated aluminum alloys under immersion. This could indicate that the coatings containing  $\text{Na}_2\text{MoO}_4$  with the water-core contained defects that allowed electrolyte to directly contact the surface of the AA2024-T3 panel. It is interesting to note, that after an initial decrease in the low frequency impedance, the samples then showed an increase in the low frequency impedance indicating improved corrosion protection.

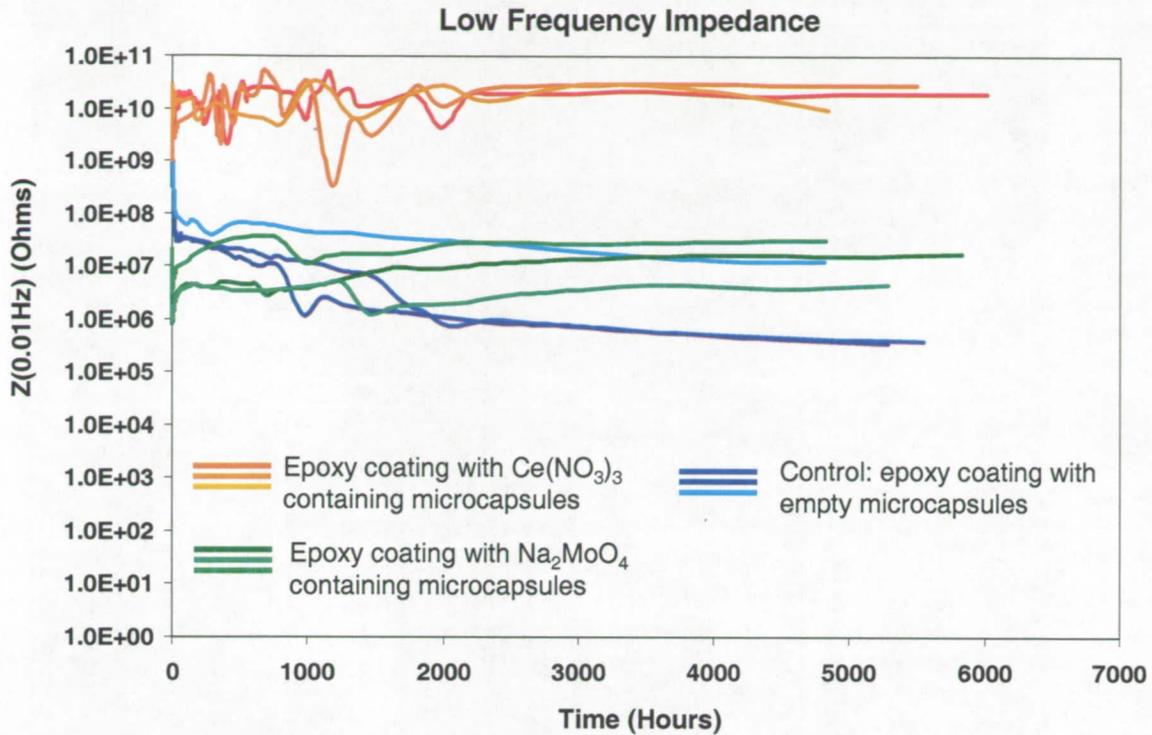


Figure 14. Low frequency impedance for coatings with incorporated dried microcapsules; Blank oil-core, water-core microcapsules containing  $\text{Ce}(\text{NO}_3)_3$  and  $\text{NaMoO}_4$ .

Scribed samples placed in ASTM B117 neutral salt spray cabinet were periodically withdrawn to make a visual assessment. Figure 15 shows images of the epoxy coating, the epoxy coating with empty microcapsules and the epoxy coating with microcapsules containing  $\text{Ce}(\text{NO}_3)_3$  after B117 exposure. The microcapsules were present in a 40% loading by weight. The control coating and coating with empty microcapsule controls both show more signs of corrosion, relative the coating with  $\text{Ce}(\text{NO}_3)_3$  microcapsules.

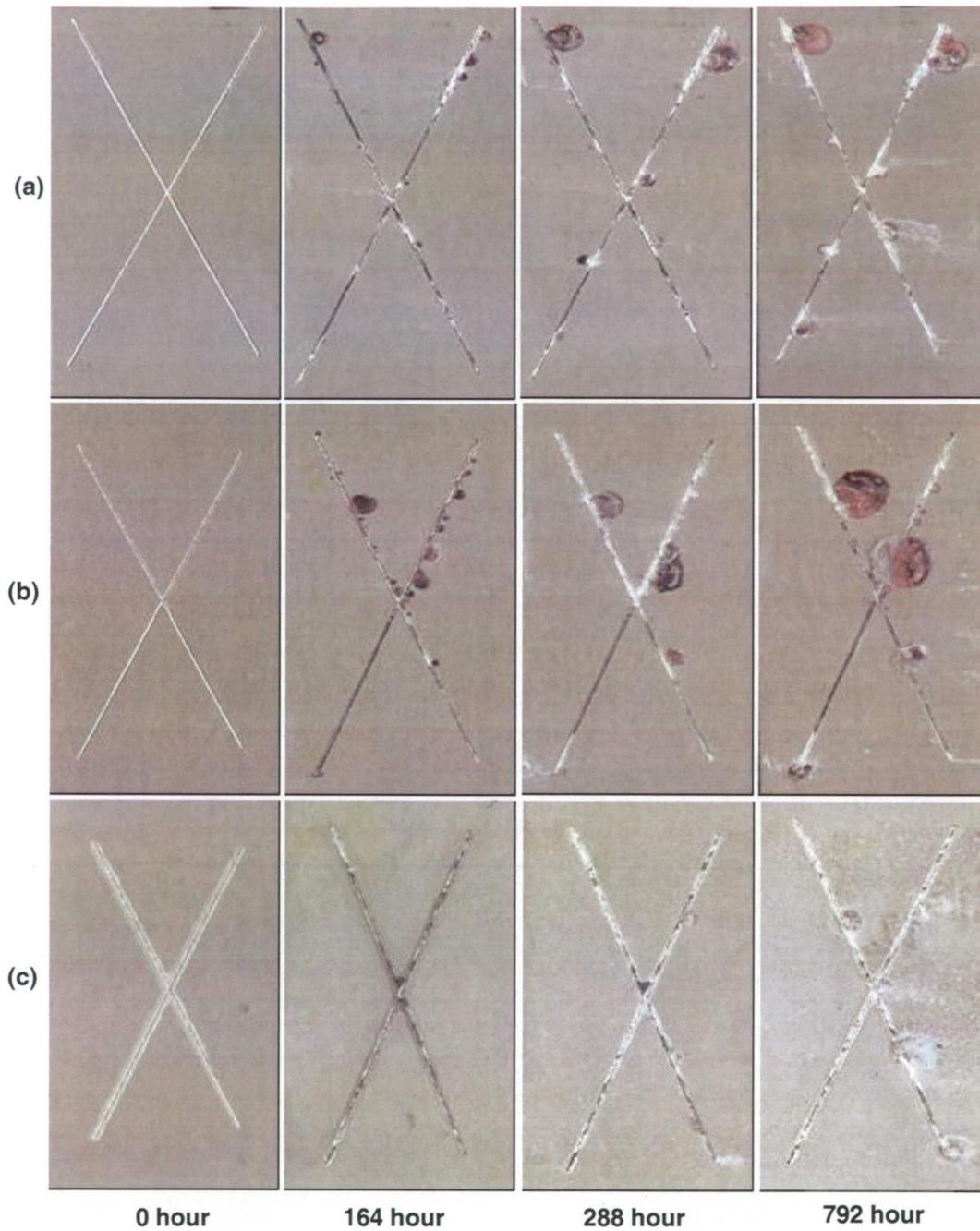


Figure 15. Scanned pictures of the remade a) epoxy amine control coating, b) epoxy amine control with 40% blank microcapsules, and c) the control coating with 40%  $\text{Ce}(\text{NO}_3)_3$  on the sandblasted AA2024 Aluminum panels.

## SUMMARY, CONCLUSIONS, AND FUTURE PLANS

A smart coating system based on pH sensitive microcapsules is being developed for early corrosion detection, corrosion inhibition, and self-healing functions. Various pH sensitive microcapsules with oil or water cores were synthesized through interfacial polymerization reactions in an emulsion. The microencapsulation process was optimized to obtain monodispersed, small microcapsules in suspension and in free-flowing powder form. The controlled release properties of these microcapsules were verified under basic pH condition and in real time showing the onset of corrosion.

The compatibility of the microcapsules with different paint systems was investigated. It was found that oil-core microcapsules are compatible with water based paints while water-core microcapsules are compatible with solvent based paints. Microcapsules were successfully incorporated into a two-part epoxy amine coating with good dispersion. Adhesion, electrochemical and salt spray testing all showed promising results for coatings formulated with inhibitor containing microcapsules. At this point in the study, a beneficial effect is observed by the corrosion inhibiting microcapsules containing either cerium cations or molybdate anions. It appears that the  $\text{Ce}(\text{NO}_3)_3$  water-core microcapsule coating out-performs the other coating systems as determined by EIS.  $\text{Ce}(\text{NO}_3)_3$  containing microcapsules also performed well in B117 testing compared to the controls.

## REFERENCES

1. W. Li and L. M. Calle, pH and Electrochemical Responsive Materials for Corrosion Control Applications (Invited), NACE Corrosion 2008, New Orleans, LA, March 2008.
2. J. Zhang and G.S. Frankel, *Corrosion* 55, 957 (1999)
3. R. E. Johnson and V. S. Agarwala, *Mater. Performance*, 33, 25 (1994)
4. H. S. Isaacs, G. Adzic, and C. S. Jeffcoate, *Corrosion* 56, 971 (2000)
5. G. S. Frankel, R. G. Buchheit, and J. Zhang, US Patent Appl. US2003/0068824.
6. O. B. Miled, D. Grosso, C. Sanchez, and J. Livage, *J. Phys. Chem. Solids* 65, 1751 (2004)
7. W. Feng, S. H. Patel, M-Y. Young, J. L. Zunino III, and M. Xanthos, *Adv. Polym. Tech.* 26, 1 (2007)
8. M. G. Durrett, R. E. Johnson, and V. S. Agarwala, ICI, Intelligent corrosion indicator, and its use for the early detection of corrosion on aluminum alloy surfaces by fluorescence, *Corrosion/2000*, Paper No. 00285
9. D. E. Bryant and D. Greenfield, *Prog. Org. Coatings* 57, 416 (2006)
10. <http://en.wikipedia.org/wiki/Fluorescein>
11. M. Alodan and W. H. Snyder, *J. Electrochem Soc.* 144 (1997), L282-L284
12. L. K. white, R. B. Comizzoli, C. A. Deckert, and G. L. Schnable, *J. Electrochem. Soc.* 128,953 (1981)

13. S-M. Li, H-R. Zhang, and J-H Liu, *T. Nonferr. Metal. Soc.* 16, S159 (2006)
14. A. C. Gutierrez and M. H. Gehlen, *Spectrochim. Acta, Part A* 58, 83 (2002)
15. J. Medina Escriche and F. Hernandez Hernandez, *Analyst* 110, 287 (1985)
16. S. Szunerits and D. R. Walt, *Anal. Chem.*, 74, 886 (2002)
17. M.P. Sibi and Z. Zong, *Prog. Org. Coat.* 47, 8 (2003)
18. <http://smaplabori.uah.edu/lce/agarwara.pdf>
19. M. Rohwerder and A. Michalik, *Electrochimica Acta*, Article in Press.
20. J. N. Barisci, T. W. Lewis, G. M. Spinks, C. O. Too and G. G. Wallace, *J. Intell. Mater. Syst. Struct.* 9, 723 (1998)
21. P. J. Kinlen, V. Menon and Y. Ding, *J. Electrochem. Soc.* 146, 3690 (1999)
22. M. Kendig, M. Hon and L. Warren, *Prog. Org. Coat.* 47, 183 (2003)
23. G. Paliwoda-Porebska, M. Stratmann, M. Rohwerder, K. Potje-Kamloth, Y. Lu, A.Z. Pich and H.-J. Adler, *Corros. Sci.* 47, 3216 (2005)
24. R. Cook, J. Elliott and A. Myers, *Tri-Service Corrosion Conference 2005*, Orlando, FL, November 14-18, 2005.
25. M. R. Kessler, *Self-healing: a new paradigm in material design*, *Proc. IMechE Vol. 221 Part G: J. Aerospace Engineering*, page 479-495 (2007)
26. Magnus Andersson, Gerald O. Wilson, Scott R. White, *Evaluation of Self-Healing Polymer Chemistries for Application in Anti-Corrosion Coatings*, *American Coatings Conference 2008 at Charlotte, NC* (June 2-4, 2008).
27. Soo Hyoun Cho, PhD Thesis "Polydimethylsiloxane-Based Self healing Composite and Coating materials", University of Illinois at Urbana-Champaign, Urbana IL (2006).
28. A. Kumar, L. D. Stephenson, and J. N. Murray, *Self-healing coatings for steel*, *Progress in organic coatings*, 55, 244-253 (2006)
29. W. Li and L. M. Calle, *Controlled Release Microcapsules for Smart Coatings*, *NACE Corrosion 2007*, Paper 07228, Nashville, TN, March 2007
30. W. Li and L. M. Calle, *A smart coating for the Early Detection and Inhibition of Corrosion*, *Proceeding of the Smart Coatings 2007*, p.191, Orlando, Florida, February 2007
31. <http://www.corrosion-club.com/paintcomponents.htm>